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(54) LIPSTICKS

We, L'OREAL, a French Body Corporate, of 14 Rue Royale, Paris 75008, France, do hereby declare the invention, for which we pray that a patent may be granted 5 to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a new cosmetic composition for making-up, which

is in the form of a lipstick.

We have already proposed to use, for the production of make-up products and especially of lipsticks, certain polymers and especially homopolymers of vinyl esters or acrylic esters, as well as copolymers of vinyl esters.

In fact, it has been found that using a certain percentage of such polymers in these products, it is possible to improve the firmness of the sticks, and to impart gloss and better adhesion as well as good persistence of the film deposited on the lips.

However, these lipstick compositions exhibit certain disadvantages, especially a 25 migration of the dyestuffs into the corners

of the lips. We have now found, according to the present invention, that it is possible to avoid or reduce these disadvantages, which affect the aesthetic appearance, by linking the polymers previously proposed with a particular type-of-glyceryl-ester-ether-or-glycol ether. In fact, by the combined use of these materials in a lipstick it is possible to

prevent the migration of the dyestuffs into the corners of the lips and moreover further to increase the gloss of the film thus deposited on the lips.

(11)

The present invention provides a lipstick

which essentially contains:

(i) at least one lipo-soluble polymer containing vinyl ester-derived units,

(ii) at least 10% by weight of 1-docosanoyloxy - 3 - (2 - ethyl) - hexyloxy propan-2-ol or a product of the average formula:

- CH₂ - CH - 0 -

in which R represents the radical derived from the alcohols of lanolin (lanolin alcohol), R' represents $C_{10}H_{21}$ and n is a number, especially about 1.5, i.e, a product obtained by reacting 11,12-epoxydodecane with lanolin alcohol,

(iii) at least one fatty substance and (iv) at least one non-toxic dyestuff.

1-docosanoyloxy-3 -(2-ethyl) -The hexoxy-propan-2-ol which, in admixture with the polymer, prevents the migration of the dyestuffs into the corners of the lips, and has the following formula:

C₂₁H₄₃—COO—CH₂—CH—CH₂—O— CH₂—CH—C₄H₉

This compound, which is novel can be obtained by reacting behenic acid (or docosanoic acid) with glycidyl 2-ethyl-hexyl ether. The reaction is suitably carried out in the presence of a basic catalyst such as sodium methylate or sodium ethylate and at a temperature of the order of 130°C for, say, 2 to 8 hours.



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The product can be isolated from the reaction mixture after several washes with water and after neutralisation with a base, and is then dried under reduced pressure. The volatile products can be removed at about 130°C/10⁻³ mm Hg and the desired product can then be distilled at about 205°C/10⁻³ mm Hg. This product is solid at ambient temperature and has a final melting point of the order of 35° to 40°C.

The products of formula (I) which likewise prevent the migration of the dyestuffs can be obtained by reacting 11,12-epoxy-dodecane with lanolin alcohol in the presence of boron trifluoride (BF₃). The reaction is conveniently conducted at a temperature of about 80°C for, say, 1 to 2 hours. The product can be isolated after neutralisation and washing with water.

The product in which n is about 1.5 is novel; it is in the form of a slightly yellow soft wax having a melting point of about 40°C.

As indicated above, the 1-docosanoyloxy - 3 - (2-ethyl) - hexoxy-propan-2-ol or product of formula (I) is present in the composition at a concentration of at least 10% but preferably 10 to 30% (by weight).

These compounds partly replaces the

These compounds partly replaces the fatty substance which may be either a wax, an oil or a mixture of a wax and an oil.

According to this invention, the fatty substance is generally present in an amount from 35 to 75%.

Amongst the waxes which can be used as the fatty substance, there may in particular be mentioned ozocerites, lanolin, lanolin alcohol, hydrogenated lanolin, acetylated lanolin, lanolin wax, beeswax, candellila wax, micro-crystalline wax, carnauba wax, cetyl alcohol, stearyl alcohol, spermaceti, cacao butter, the fatty acids of lanolin, petrolatum, white petroleum jellies, monoglycerides, diglycerides and triglycerides which are solid at 25°C, fatty esters which are solid at 25°C, silicon waxes such as methyloctadecanoxy-polysiloxane (dimethylsiloxy) and poly stearyl monostearoxysiloxane, ethanolamide, colophony and its derivatives such as glycol abietate and glycerol abietate, hydrogenated oils which are solid at 25°C, sucro-glycerides and the oleates, myristates, lanolates, stearates and dihydroxy-stearates of calcium, magnesium, zirconium and aluminium.

Amongst the oils which can be used as fatty substances there may in particular be mentioned paraffin oil, purcellin oil, perhydrosqualene, sweet almond oil, avocado oil, calophyllum oil, castor oil, caballine oil, lard oil, olive oil, mineral oils having a boiling point of 310 to 410°C, silicone oils such as dimethylpolysiloxanes,

linoleyl alcohol, linolenyl alcohol, oleyl alcohol, cereal germ oil such as wheat germ oil, isopropyl lanolate, isopropyl palmitate, isopropyl myristate, butyl myristate, cetyl myristate, hexadecyl stearate, 2-ethylhexyl stearate, butyl stearate, octyl hydroxy stearate, decyl oleate, acetyl-glycerides, octanoates and decanoates of alcohols and of poly-alcohols such as of glycol and glycerol, ricinoleates of alcohols and of poly-alcohols such as cetyl ricinoleate, isostearyl alcohol, isocetyl lanolate, isopropyl adipate, hexyl lanolate and octyl-dodecanol.

It is also possible to use as waxes or as oils, according to the invention, the derivatives of 1,2-alkanediols and especially the esters of 1,2-alkanediols with fatty acids such as those described in our British Specification No. 1,514,287 or one of the compounds described in British Specification Nos. 1,431,153 and 1,516,195.

The polymers having vinyl ester units which can be used in the lipsticks according to the present invention must be liposoluble, that is to say must have a high affinity for waxes and oils. As indicated above, these polymers are either homopolymers or copolymers and are generally present in the composition at a concentration of 10 to 35% by weight. Amongst the homopolymers there may in particular be mentioned those resulting from the homopolymerisation of vinyl hexanoate, of vinyl 2,2-dimethylpentanoate, of vinyl octanoate, of vinyl cekanoates (cekanoic acid being the tradename of a mixture of linear and branched fatty acids having the same number of carbon atoms, namely 8, 9 or 10), of vinyl laurate, of vinyl stearate and of vinyl isostearate.

Amongst the copolymers, there may in particular be mentioned those resulting from the copolymerisation of vinyl acetate with allyl stearate, of vinyl acetate with vinyl laurate, of vinyl acetate with vinyl stearate, of vinyl acetate with octadecene, of vinyl acetate with octadecyl vinyl ether, of vinyl propionate with allyl laurate, of vinyl propionate with vinyl laurate, of vinyl stearate with 1-octadecene, of vinyl acetate with-1-dodecene, of -vinyl-stearate-withethyl vinyl ether, of vinyl propionate with cetyl vinyl ether, of vinyl stearate with allvl acetate, of vinyl 2,2-dimethyl-octanoate with vinyl laurate, of allyl 2,2-dimethyl-pentanoate with vinyl laurate, of vinyl dimethylpropionate with vinyl stearate, of allyl dimethylpropionate with vinyl stearate, of vinyl propionate with vinyl stearate, of vinyl dimethylpropionate with vinyl laurate and of allyl propionate with allyl stearate.

These copolymers can optionally be crosslinked by means of a crosslinking agent, which has the effect of increasing the

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3∵	1,505,000		
	crosslinking agents there may in particular mol	g of behenic (or docosanoic) acid (1.050 s) which have been fused in a flask, and temperature is then raised to 130°C	55
٠.	The state of the s	an nitrogen	
	divinyioonzono, - i i i i i i i i i i i i i i i i i i	haraster 186 o (1 mol) of 2-ethyllicky	
	_1	cidyl ether are added dropwise, whilst	70
735	octadecanedioate.	ring, and after the end of the addition the	
	Preferably these homopolymers and stir	ring, and after the end of the addition	
	conclumers have a molecular weight of this	sture is heated under nitrogen for 6 hours	
		130°C.	
۱۸ :	2,000 to 300,000 and processes	The extent of the reaction is determined	75
IV	300,000.	measuring the residual acid number. The	75
1	These homopolymers and copolymers of by	action is continued until the degree of	
	vinyl esters are described in detail in our rea	ection is continued	
	British Specifications Nos. 1,476,194 and con	nversion is about 95%. The product thus obtained is washed once	
	-1-476.195.	The product thus obtained is washed one	
15	The dvestuffs employed in the will	th 500 ml of boiling water containing the	80
	the state of the invention are am	iount of sodium hydroxide required to	00
1	"Tompositions and those used no	utralise the residual acidity.	
	Of Course in general	After the water, 200 ml of isopropanol are	
	commonly in lipsticks. They are in general	ded to improve the phase separation. The	
	massent in an amount Iron 2 to 30/0. au	oduct is then washed twice with water at	
20	Amongst them there may be illelitibled the	oduct is tilell washed twice with	85
A ^O	eneing and other halogenated derivatives of ou	°C (about 500 ml per wash).	
		The product is then dried in vacuo, whilst	
		rring, on a boiling waterbath.	
	Red No. 21, D and C Red No. 27 and D and	Thereafter, the product is purified by	
		alegular distillation	
25		1) The volatile products are removed at	90
	iron oxides, chromium oxides, ultramarines	30°C under 10 ⁻³ mm Hg	
	(molecularides of aminosilicates), titalium	2) The product is distilled at 205°C under	
٠.	Migrides, and organic pigments such as D	2) The product is distinct at 205 C and 5	
• • •	and C Red No. 36 and D and C Orange No. 10) ⁻³ mm Hg,	
20		Distillation yield: 78%	0.5
30	Finally, amongst the dyestuffs there may	Overall yield: 67%	95
	also be included the lakes such as the	•	
	also be included the lakes such as the	nalyses:	
		Saponification number:	
	and 27, the barium lakes of D and C Red	theory: 1.98 milliequivalents/g	
35	No K and Q the Alliakes of D and C Red	theory, 1.76 millioguivalents/g	
	1 No. 21 and 7/ and 1) and C I click 190. 3	found: 2.0 milliequivalents/g	100
	and 6 and the zirconium lakes of D and C	Hydroxyl number:	100
	Red No. 21 and of D and C Orange No. 5.	theory: 1.98 milliequivalents/g	
	Red 140. 21 and 0. 2 and 10 according to	found: 1.85 milliequivalents/g	
	Of course, the compositions according to	Acid number: zero	
4	the invention can also contain other	Final melting point: 35°C.	
	conventional ingredients such as, for	I mai morning t	
- :	avample nearlescent agents, suitably in an	Preparation of a product of formula (I)	105
	amount of 2 to 20%, periumes, and-sunoun	5.2 ml. of a BF ther complex was added	
	egents antioxidants and Drescivatives.	7.2 IIII. Of a Difference complex has added	
	Suitable pearlescent agents include	to 740 g (2 mols) of lanolin alcohol which	
. 4	bismuth oxychloride, mica-, titania and	had been previously melted at about 80°C.	
١.	Districting Oxychiotics, initial,	see a 12 mais of 11.12-epoxydouecane is	110
• • •	ouanine crystais.	then added drop by drop over about I nour.	110
	Amongst the anti-oxidants	The temperature is maintained at out. It	
	particular be mentioned those of the	shout in minutes after the end of the	
. 5	of the lie terms strok at the DEODVI. Outvi duu	addition to ensure that all the epoxide	
	Andervi esters of gaille acid, butylated	added has been consumed.	
	hydroxyanisole, butylated hydroxy-toluene	The product thus obtained is washed with	115
 :	and nordihydrogualarette actu.	- Ine-product thus obtained is washed wash	- 175
:	In certain cases, it is also desirable or	water containing the necessary quantity of	
	In Certain cases, it is and cents for the	soda to neutralise the acidity due to the	
	necessary to use certain solvenis	presence of the catalyst. The organic phase	
:	dyestuffs which are insoluble in the latty	separated after decantation is washed again	
:	substances. Amongst these solvents there	three times with hot water.	120
١.	may be mentioned the glycois, the	The product is then taken up in its own	
	tetrahydrofurfuryl esters, the polyethylene	weight of water and the material distilled to	
	60 glycols and the monoalkanolamides.	Weight Of water and the material and then the	;
; '		eliminate extracted impurities and then the	
	Preparation of 1 - docosanoyloxy - 3 - (2 -	product is dehydrated completely under	126
	ethyl) - hexoxy - propan 2 ol	reduced pressure.	123
	ciliyi - licxoxy - propan 2 or	One thus obtains a product of formula (1)	,
	2.9 g of sodium methylate powder (50	in the form of a soft slightly yellow wax.	•
	milliequivalents) are added, whilst stirring, to		

Example 3 A lipstick is prepared, according to the invention, by mixing the following ingredients:

1.5 g 1.5 g

0.8 g

100 g

Calcium lake of D and C Red 6

Al lake of D and C Yellow 6

D and C Red 36

Perfume

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Example 5 A lipstick is prepared, according to the invention, by mixing the following ingredients:

Al lake of D and C Yellow 6

Bi oxychloride

Perfume

g

g

g

12 .

1 g 110

100

	5		1,569	,009	5
	5 1	Dzocerite Microcrystalline wax Acetylated lanolin Castor oil Hydr genated coconut oil Lanolin alcohols Compound of the formula R—COOCH ₂ —CH—R'	4 g 6 g 10 g 10 g 10 g 3.9 g	Colorants: Titanium oxide Al Laque D and C red 21 Ca Laque D and C red 7 D and C red 6 Yellow iron oxide Black iron oxide Al Laque D and C yellow 5 Perfume	3 g 1 g 50 0.2 g 2.5 g 1.1 g 0.35 g 4.5 g 55 0.5 g
:		он			100 g
	10	R=C ₁₈ H ₃₁ Melting point 55—60°C R'=C ₁₂ /C ₁₄ Acid number 0.02 milliequivalent/g Butylated hydroxytoluene Copolymer of 31.3% of vinyl acetate and 68.7% of allyl stearate Homopolymer of vinyl laurate 1 - Docosanoyloxy - 3 - (2 - ethyl) - hexoxy - propan - 2 -	0.1 g 8 g 16 g	Example 7 A lipstick is prepared by m following ingredients: Polyvinyl laurate Polyethylene grease (MW= 1,500) 1 - Docosanoyloxy - 3 - (2 - ethyl) - hexyloxy - propan - 2 - ol	9.2 g 33 g 65
		ol	15 g	Compound of the formula:	_
•	20	Colorants Titanium oxide Ca lake of D and C Red 7 D and C Red 36 Black iron oxide	6.5 g 0.5 g 0.5 g 0.4 g	OH R=C ₀ H ₀ W ₀ W ₁ = noint_55 6	4 g
i i	26.	Al lake of D and C Yellow 5	2.6 g 0.5 g		70
	30	Example 6 A lipstick is prepared by mit following ingredients: Polyvinyl laurate Copolymer of 31.3% of vinyl	100 g	Lanolin Liquid lanolin Amyl paradimethylamino- benzoate D-panthenol Calendula oil	9.7 g 10.5 g 1 g 1 g 75 8 g 2 g 0.1 g 3 g
		acetate and 68.7% of allyl stearate	8.75 g 8.75 g	9	80
:	35	Microcrystalline wax Di-tertiarybutyl para-cresol Product of formula (I) such as prepared in the Example above	0.1	Al Laque D and C red 21 D and C red 6 Yellow iron oxide	0.2 g 0.5 g 0.3 g 0.4 g 2.5 g 85
:		Compound of the formula:		Perfume	0.6 g
	40	R—COOCH ₂ —CH—R' OH	4.35	gExample 8	100 g
- ,		$R = C_{15}H_{31}$ $R' = C_{12}/C_{14}$ Melting point=55—60	P°C	A lipstick is prepared by following ingredients:	90
		Butyl ricinoleate Aceto glyceride Acetylated lanolin Oleic alcohol Liquid lanolin	13 4.35 4.35 4.35 4.35	g Polyethylene grease g Product of formula (I) such a g prepared in the abov	7 g 27 g s e 9.5 g 95
	1 % 1 %			π	

	Compound of the formula:		(ii) at least 10% by weight of 1 -	50
	•	3.5 g	docosanoyloxy - 3 - (2 - ethyl) - hexyloxy - propan - 2 - ol or a product obtained by	30
	R—COOCH ₂ —CH—R'	3.3 g	reacting 11,12-epoxydodecane with the	
	ÓН		alcohols of lanolin,	
			(iii) at least one fatty substance and (iv) at least one non-toxic dyestuff.	55
	$R = C_{15}H_{31}$		2. A lipstick according to claim 1 in which	
	$R'=C_{12}/C_{14}$		the polymer is a homopolymer of vinyl	
5	Lanolin	9.0 g	hexanoate, vinyl 2,2-dimethyl-pentanoate,	
	Acetylated lanolin	9.5 g	vinyl octanoate, vinyl cekanoates, vinyl laurate, vinyl stearate or vinyl isostearate.	60
	Mineral oil	9.5 g 3.5 g	3. A lipstick according to claim 1 in which	
	Polyethylene wax Tertiary-butyl anisole	0.1 g	the polymer is a copolymer of: vinyl acetate	
10	Butyl ricinoleate	6.4 g	with allyl stearate, vinyl acetate with vinyl laurate, vinyl acetate with vinyl stearate,	
	Octyl-hydroxystearate	6.5 g	vinyl acetate with octadecene, vinyl acetate	65
	Colourants		with octadecyl vinyl ether, vinyl propionate	
	Colourants: Titanium oxide	2 g	with allyl laurate, vinyl propionate with	
	Al Lague D and C red 27	2 g	vinyl laurate, vinyl stearate with 1- octadecene, vinyl acetate with 1-dodecene,	
15	Ca Laque D and C red 7	lg 3g	vinyl stearate with ethyl vinyl ether, vinyl	70
	D and C red 6 Perfume	3 g 0.5 g	propionate with cetyl vinyl ether, vinyl	
	Felluine		stearate with allyl acetate, vinyl 2,2-	
		100 g	dimethyl-octanoate with vinyl laurate, allyl 2,2-dimethyl-pentanoate with vinyl laurate,	
	Example 9		vinyl dimethylpropionate with vinyl	75
20	A lipstick is prepared by mi	xing the	stearate, allyl dimethylpropionate with vinyl	
	following ingredients:	_	stearate, vinyl propionate with vinyl	
	Polyvinyl laurate	28 g	stearate, vinyl dimethylpropionate with vinyl laurate or allyl propionate with allyl	
	Conclumer of 31.3% of vinyl		stearate.	80
	acetate and 68.7% of allyl	4.8 g	4. A lipstick according to any one of the	
25	stearate Polyothylene gresse	33 g	preceding claims in which the polymer is	
	Polyethylene grease 1 - Docosanoyloxy - 3 - (2 -		one which has been cross-linked with tetraallyloxyethane, divinylbenzene, divinyl	
	ethyl) - hexyloxy - propan -	10.2 -	octanedioate, divinyl dodecanedioate or	85
	2 - ol	19.3 g	divinyl octadecanedioate.	•
30	Compound of the formula:		5. A lipstick according to any one of the preceding claims in which the polymer is	
	R COO—CH₂—CH—R′	1 g	present in an amount from 10 to 35% by	
	R COO—CH ₂ —CH—R' OH		weight.	90
	OH		6. A lipstick according to any one of the	
	R=CurHat No. 11: 55 609	C	preceding claims, characterised in that the 1 - docosanoyloxy - 3 - (2 - ethyl) -	
	$R = C_{15}H_{31}$ $R' = C_{12}/C_{14}$ Melting point 55—60°	C	hexoxy - propane - 2 - ol or the product	•
	The state of the s	0.1 g	obtained from 11,12-epoxydode cane and	95
35	Tertiary-butyl anisole Acetylated lanolin	4.8 g	lanolin alcohol is present in an amount from	
-	Mineral oil	4.8 g	10 to 30% by weight. 7. A lipstick according to any one of the	
			preceding claims in which the fatty	
	Colourants: Al Laque D and C red 21	0.6 g	substance-is-at-least-one-wax-or-at-least-one	-100-
	D and C red 36	0.3 g	oil or a mixture of at least one wax and at least one oil.	
40	D and C red 30	0.5 g	8. A lipstick according to claim 7 in which	
	D and C red 13	0.2 g 2 g	the fatty substance is present in an amount	
	Al Laque D and C yellow 5 Perfume	0.6 g	of from 35 to 75% by weight.	105
	1 cirumo		9. A lipstick according to any one of the preceding claims in which the non-toxic	
		100 g	dyestuff is present in an amount from 2 to	
			30% by weight.	
45			10. A lipstick according to any one of the preceding claims which also contains one or	110
	 A lipstick, which contains: at least one lipo-soluble 	nolvmer	more pearlescent agents, perfumes, anti-	
	containing vinyl ester-derived un		sunburn agents, antioxidants, preservatives,	
	-			

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or solvents for the dyestuff if the latter is insoluble in the fatty substance.

11. A lipstick according to any one of the preceding claims in which the product obtained from 11,12-epoxydodecane and lanolin alcohol has the average formula:

$$R - O = \begin{bmatrix} CH_2 - CH - O \\ I \\ R^I \end{bmatrix}$$

in which R represents a radical derived from the alcohols of lanolin, R' represents $C_{10}H_{21}$ and n is about 1.5.

12. A lipstick according to any one of claims 1 to 10 in which component (ii) is 1-docosanoyloxy-3 - (2-ethyl) - hexyloxy-propan-2-ol

propan-2-ol.

13. A lipstick according to claim 1 substantially as hereinbefore described.

14. A lipstick according to claim 1

14. A lipstick according to claim 1 substantially as described in any one of Examples 1 to 9.

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